

GEOCHEMICAL AND PHYSICAL CONTROLS ON VADOSE ZONE HYDROLOGY OF HOLOCENE CARBONATE SANDS, GRAND BAHAMA ISLAND

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ABSTRACT

This paper explores the relationship between vadose zone hydrology and geochemical changes in mixed mineralogy carbonate sands from a Bahamian coastal dune of Holocene age. Cores were taken from two sites: at site A, a shallow humic Entisol is developed beneath open scrub vegetation, while at site B a deeper, more organic-rich Inceptisol has formed beneath a mature hardwood coppice. X-ray diffraction analysis reveals significant contrasts in mineralogy both within and between the two sites, with partial stabilization of high-Mg calcite and aragonite, to low-Mg calcite. Stabilization is greater at site B, and is accompanied by a significant increase in total porosity. Diagenetic changes in pore-size distribution have implications for residence times of percolating water, as determined using measurements of moisture retention characteristics using pressure plate apparatus, and hydrological models of unsaturated zone moisture flux. The diagenetically more mature sands from site B have a 50–100 per cent higher moisture retention, although unsaturated hydraulic conductivity is also higher, particularly at greater suctions. The increase in water retention is likely to enhance further rates of mineral-controlled reactions, while development of an organic-rich soil also enhances the geochemical drive for dissolution. Carbonate diagenesis thus appears to be strongly linked to vadose zone hydrology, and the interactions identified here have important consequences for the nature and long-term rates of mineral stabilization. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The effects of physical properties of soil and sediment on vadose zone hydrology have been widely studied (Hall *et al.*, 1975; Arya and Paris, 1981; Rawl *et al.*, 1982; Saxton *et al.*, 1986). The evolution of these properties, in particular grain-size distribution and porosity, over long time scales can be considerable, involving changes in permeability and moisture retained at different tensions (e.g. Brooks *et al.*, 1993). The evolution of geochemical properties of sediment has also received attention, particularly in the case of biologically and chemically precipitated sediments such as carbonates and evaporites (Land *et al.*, 1967; Gavish and Friedman, 1969; McKenzie *et al.*, 1981). However, interaction between changing geochemical properties of sediments and vadose zone hydrology has received considerably less attention. This is surprising given that comparable time scales are involved in geochemical evolution of more reactive sediments and in changing physical properties which affect hydrological behaviour.

For carbonate sediments the relationship between evolving geochemical and physical properties and sediment hydrology is of particular interest because of their susceptibility to leaching and cementation. The majority of carbonate sedimentation occurs in shallow tropical and sub-tropical seas where the sediments are inherently susceptible to any relative fall in sea-level. The resultant exposure brings the depositional mineral assemblage, dominated by metastable aragonite and magnesium-rich (high-Mg) calcite, into the meteoric realm where it is subject to profound and rapid diagenetic change.

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Transformation of aragonite and high-Mg calcite to low-Mg calcite will occur over a timescale of 1–100 ka, driven by differences in thermodynamic stability and aided by water-controlled reactions (James and Choquette, 1984). While the stabilization of high-Mg calcite is generally viewed as neomorphic, occurring without apparent loss of calcium ions in solution (Land *et al.*, 1967; Gavish and Freidman, 1969), stabilization of aragonite is frequently associated with significant porosity generation and deposition of low-Mg calcite cements either locally or further along the groundwater flow path. The porosity distribution will evolve with generation of mouldic secondary porosity and occlusion of primary porosity by cementation (Land *et al.*, 1967; Harrison, 1975). Within modern phreatic fresh and mixing zones stabilization of Holocene ooids takes place with a high overall efficiency, approximately 90 per cent of calcium carbonate being redeposited as low-Mg cements (Budd, 1988). While there are no comparable studies of vadose zone stabilization, in comparison with the phreatic zone residence times are short, and thus efficiencies may be significantly lower and porosity generation commensurately greater.

The potential for diagenetic processes to affect the relationship between soil moisture content and tension is considerable. The effective pore radius may be reduced where cements are deposited, but enlarged where dissolution of allochems is dominant. Furthermore, the contact angles between water menisci and pore walls may be increased as surface coatings develop (Hillel, 1982). Thus the hydrological effect of geochemical transformations is dependent on the net balance between loss and accumulation in the system. The pore sizes involved in water movement vary with moisture content, so changes in porosity leading to changes in retention will also affect unsaturated hydraulic conductivity. This is likely to be particularly significant in determining the distribution of dissolution and/or cementation through the profile. Little is known about the interaction between water movement and retention in pores of different size and resulting mineral transformations. However, the fabric-selective nature of cementation and small-scale porosity development was noted for the Pleistocene Miami Oolite (Evans and Ginsburg, 1987), where cementation of fine-grained sediments results in channelling of flow which effectively isolates portions of aragonite from meteoric waters.

Exposure of metastable marine carbonates to the meteoric environment occurs along tropical and sub-tropical coasts where dune ridges develop, sourced from shallow offshore waters via beaches. Such sandy sediments provide an ideal medium for hydrological studies, being relatively permeable, of relatively uniform grain size and giving rapid hydrological response as well as retaining constant porosity during laboratory testing. In this study we examine the co-evolution of geochemical and hydrological behaviour in the vadose zone of a vegetated beach ridge of Holocene age from the northern Bahamas. The objectives of this paper are firstly to examine the extent of mineral stabilization and porosity generation in the young carbonates, and secondly to investigate links between diagenesis and physical and hydrological properties. Such links have remained largely unexplored, but the integration of geochemical and hydrological properties has the potential to provide important new insights into both diagenetic evolution and chronosequence development.

THE FIELD AREA AND INVESTIGATIVE METHODS

The field study was conducted on Grand Bahama Island, on the southern margin of the Little Bahama Bank in the northern Bahamas (Figure 1). Here a low dune ridge of Holocene sands runs along most of the 100 km length of the southern coast, onlapping extensive deposits of stabilized Pleistocene limestones. The region is tectonically stable, and following the rapid rise after the last glacial maximum, sea-level has risen steadily over the last 3.5 ka at 3.5–4 cm/100 years (Boardman *et al.*, 1989). Grand Bahama has a 'tropical marine climate' characterized by relatively dry winters with occasional cold fronts from the American continent, and summers dominated by persistent northeasterly trade winds which generate frequent convective rainfall. Mean daily temperatures range from 18°C in winter to 28°C in summer, and the annual rainfall averages 1355 mm, with over 25 per cent of this derived from hurricanes and tropical storms. Rates of potential evaporation derived from open-pan measurements and Penman calculations average 1600 mm a⁻¹, but actual evapotranspiration has been estimated as 25 per cent of the mean annual rainfall for the Pleistocene limestones (Whitaker and Smart, *in press*).

The study area is situated within the Lucayan National Park on the southern shore of the island, and comprises a beach ridge, some 100 m wide and reaching a maximum elevation of 4 m adjacent to the beach.

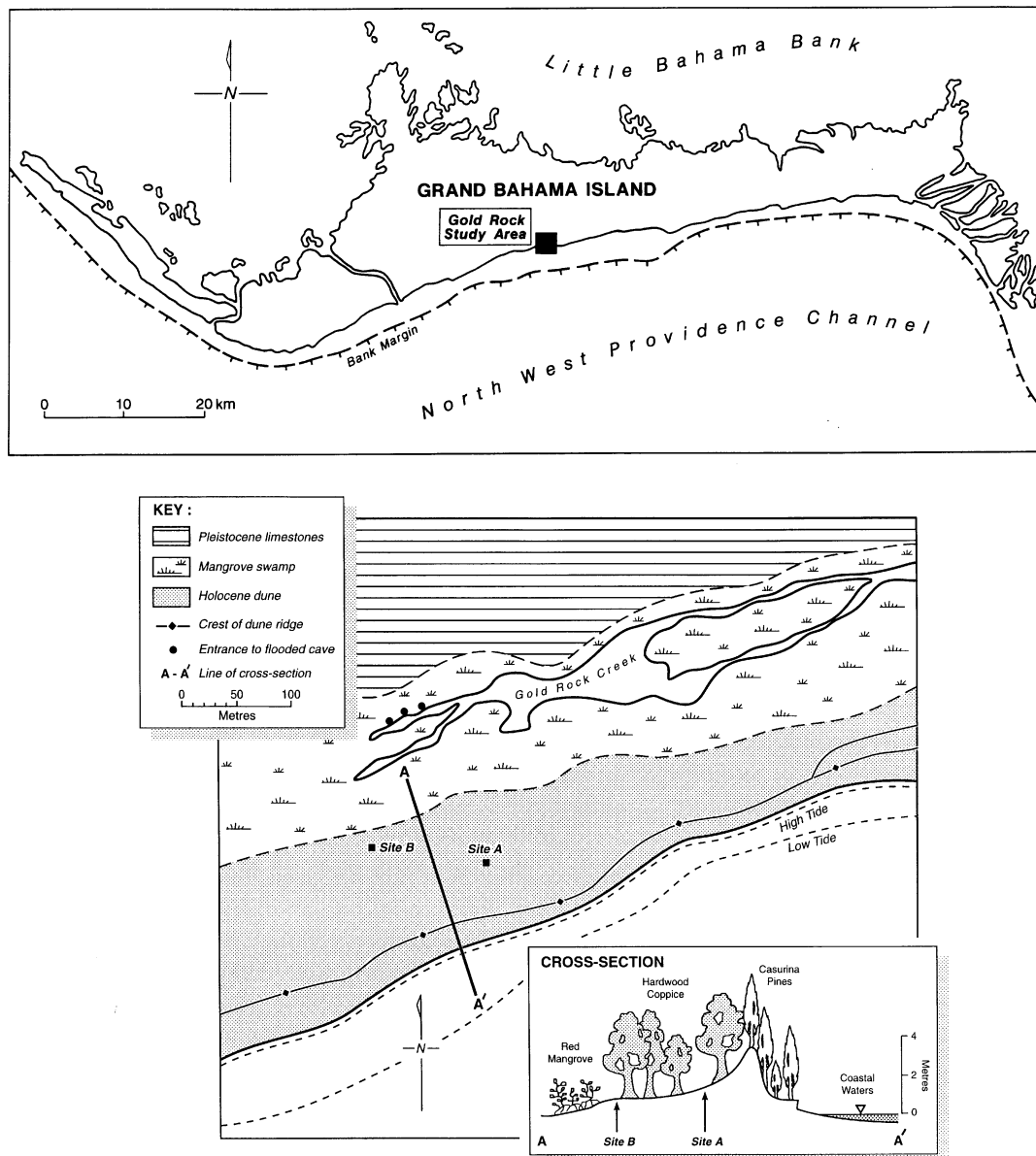


Figure 1. (A) Location of the Gold Rock study area on Grand Bahama Island, Little Bahama Bank. (B) Sketch map showing location of sample sites and cross-section (inset) showing relationship with dune topography and distribution of vegetation types

Behind this dune barrier, water draining from the large freshwater lens developed in the Pleistocene limestones, largely *via* cave passages, forms the brackish (18–20 ppt salinity) Gold Rock Creek which opens to the sea almost 3 km further to the east (Whitaker, 1992). Most of the creek is densely vegetated with Red Mangrove (*Rhizophora mangle*), and the shallow creek bed is mantled by fine-grained recent carbonate muds. Within the Holocene sands 12 m from the creek the water table lies within 70 cm of the ground surface (site B, Figure 1B), but fluctuates semi-diurnally in phase with creek water levels. The salinity of the ground water averages 7.6 ppt, and the waters are organic-stained and anoxic, emitting a strong H_2S odour. Progressing seawards, the ground elevation increases, the depth of the vadose zone exceeding 1.0 m at 50 m from the creek (site A, Figure 1B). There is clear zonation of vegetation across the dune ridge, from the mangrove swash of the creek, through open

mature hardwood coppice on the low back dune, to more sparse woodland of Australian Pine (*Casuarina* spp.) along and seaward of the dune crest.

The humic protocols developed on the sands are ubiquitous throughout the archipelago in such environments, and are termed 'Whiteland Soils' by Little *et al.* (1977). They are grey/pale, mineral-deficient regosols with an A1 horizon of variable thickness which is little more than a small amount of organic matter incorporated into the calcareous sands. Within the dune ridge two contrasting sites were selected. Site A is located on the landward side of the main dune ridge, 45 m from the back of the beach at an approximate elevation of 1.5 m. The relatively open scrub includes Sea Grape and Pigeon Plum (*Coccoloba uvifera* and *C. diversifolia*). Coco ground cover of Sea Oats (*Uniola* spp.). The well-decomposed litter, 5–7 cm thick, is poorly integrated with the underlying sands, which showed little evidence of gross organics, although a number of fine roots were present to a depth of 20–30 cm. The core reached a total depth of 90 cm, penetrating freely draining material with no evident stratification.

The second site, site B, is located further inland and some 12 m from the creek margin, as defined by the limit of mangrove growth. Here the mature hardwood coppice is dominated by Giant Poisonwood (*Metopium toxiferum*), with Cinnecord (*Acacia oriophylla*), White Stopper (*Myrsine forlidana*) and Cabbage Palm (*Sabal palmetto*). These give rise to a relatively thin litter cover <5 cm deep, with organics incorporated into the underlying sands to a maximum cored depth of 75 cm. The soils are much browner in colour (10YR3/2 compared to 10YR5/2 for site A), the large roots (not observed in excavations for core A) were present to a maximum excavated depth of 80 cm. At this site the activity of numerous burrowing land crabs was apparent. Although dry at the surface, a clear wetting front appeared at a depth of 25 cm, extending down to the water table at 70 cm depth. At both sites soil $p\text{CO}_2$ was measured using a Miotke Soil CO_2 probe with gas analyser tubes.

The two cores were taken by inserting robust sections of 9 cm diameter plastic pipe to depths of 90 cm and 80 cm for core A and core B respectively, causing minimal compaction. These were then extracted by digging away the surrounding sediment. The cores were drained, securely packaged and returned to the laboratory for analysis. The sediment was progressively extruded, causing minimal compression, and two 4.5 cm diameter plastic rings were used to provide paired sets of samples covering depth increments of 3 cm. One set of small cores was retained for future thin-section analysis, the second set was used for analysis of hydrological properties, and residual sediment was collected for mineralogical and geochemical analysis and particle-size measurement.

The mineralogical composition of the sands was determined by X-ray diffraction (XRD), scans from 25 to 32° showing clear peaks for aragonite, high-Mg and low-Mg calcite, with trace amounts of dolomite. Peak areas were used to calculate mineralogical fractions, with aragonite as an internal standard and using the standard curve of Milliman (1974). Reproducibility was better than 5 per cent. Mole percentage of magnesium in the high-Mg calcite was determined by the method of Goldsmith *et al.* (1961). Extracts prepared by HCl dissolution and filtration through 0.45 μm filter papers were analysed by atomic absorption spectrophotometry for strontium and magnesium, which showed good agreement with XRD data. The sediments proved extremely pure, with an average acid-insoluble residue of less than 0.5 per cent. Percentage organic matter (by weight) was obtained using the Walkley-Black method, and particle-size distribution curves (63–2000 μm size range) were obtained using dry sieving.

Hydrological properties of the sands were measured using pressure plate apparatus. The samples were brought to equilibrium at suctions of 10, 20, 50, 75, 90, 120, 200 and 900 cm, initially using a hanging column of water, but the higher suctions being produced using compressed gas. The saturated hydraulic conductivity of each sample was then measured using a constant-head permeameter. Finally, the samples were dried and weighed to produce values for the bulk density. Porosity was derived from bulk density assuming a specific gravity for the carbonates of 2.72 g cm^{-3} . From the bulk density and sediment weights at different suctions, the soil moisture retention curve for the drying cycle was obtained for each sample.

DIAGENESIS OF THE CARBONATE SANDS

To assess the extent of mineral stabilization which has occurred, the composition of the two cores was

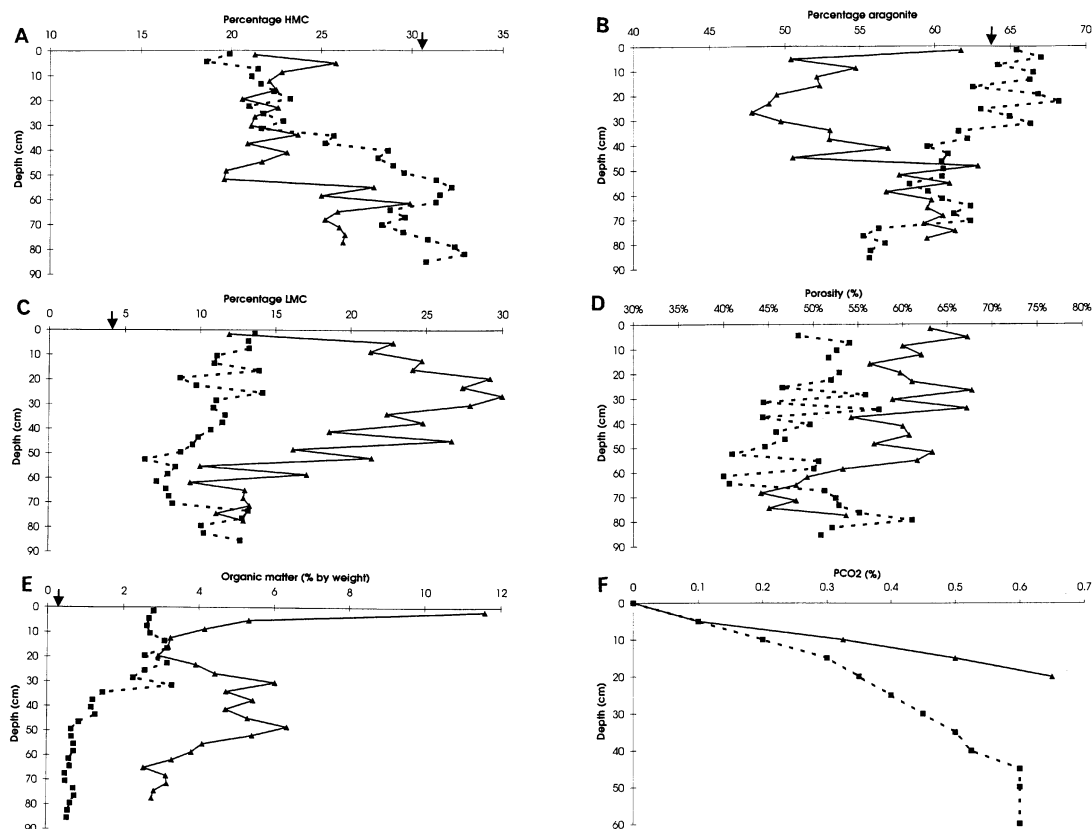


Figure 2. Vertical variation of geochemical and physical properties of the cores. Core A is broken line, core B is solid line: arrows show mean value for samples of modern beach sands

compared with recently deposited sands from the modern beach. In the absence of large-scale spatial and temporal variations in vadose zone diagenetic efficiency, the extent of dissolution of high-Mg calcite and aragonite should be directly proportional to the low-Mg calcite produced by stabilization of aragonite. On average, the ratio of high-Mg calcite:aragonite:low-Mg calcite of core B is 0.24:0.56:0.20, while core A has a ratio of 0.27:0.62:0.11. The higher proportion of low-Mg calcite in core B indicates that mineralogical stabilization has progressed further than in core A. However, sediment on the modern beach has a mineralogical ratio of 0.31:0.65:0.04, suggesting that both cores have evolved significantly when compared to the probable composition of the source material.

The variation in mineralogy with depth is shown in Figure 2A–C, with modern beach sands for comparison. All percentages are expressed here as fractions of the total carbonate. It should be noted that whilst the range of compositional variation is only 10–25 per cent, depth distributions within both cores appear to show internal consistency to ± 2 –4 per cent and thus we can interpret relatively minor variations with reasonable confidence.

In the lower part of core B (>55 cm depth) high-Mg calcite represents 26 ± 2.8 per cent of the total carbonate fraction, which is significantly lower than the beach sands, but higher than the young overlying section of B which comprises 22 ± 1.5 per cent high-Mg calcite (Figure 2A). Within the upper section, high-Mg calcite decreases slightly with depth, but below this no systematic variation is evident. Core A also appears to comprise an upper and a lower section with statistically distinctive mineralogical composition. Below 63 cm, core A has a high-Mg calcite content of 30 ± 16 per cent, with a trend to lower values at depth. Assuming an initial sediment composition similar to that of the modern beach, diagenesis appears to have had little impact on the high-Mg calcite in this section. In the upper part of core A there is a marked reduction in high-Mg calcite towards the surface, reaching a minimum of less than 19 per cent indicating considerable stabilization at shallow depth.

Considering the aragonite distribution (Figure 2B), the two distinct sections are again apparent in both cores. Within core B, the lower section is characterized by 59 ± 1.5 per cent aragonite, invariant with depth and significantly lower than the probable initial composition. In contrast, the upper section has 53 ± 4.6 per cent aragonite, the large standard deviation reflecting much greater stabilization in the central part (17–47 cm depth). Whilst in core B the distribution of aragonite is broadly similar to that of high-Mg calcite, the two minerals appear to vary independently in core A. The lower section has significantly less aragonite than the upper sections, 58 ± 3.2 per cent and 63 ± 3.0 per cent respectively, and in the upper 32 cm does not differ significantly from the modern beach sands. Furthermore, aragonite content decreases significantly with depth, in opposition to the trend for high-Mg calcite.

Overall, mineral stabilization has progressed further in core B than in core A, with the upper part of core B having been most strongly affected. The inverse relationship between high-Mg calcite and aragonite in core A is of particular interest, possibly suggesting that differing environmental conditions control the diagenetic susceptibility, although original depositional variation in the grain composition and/or type may also be important. The positive co-variation of high-Mg calcite and aragonite in core B is in marked contrast and may reflect the higher degree of stabilization, possible because of a more chemically aggressive environment.

All samples are significantly enriched in low-Mg calcite, the major product of mineralogical stabilization, compared with modern beach sands (Figure 2C). The greater diagenetic maturity of core B is very clear, with maximum values for low-Mg calcite of almost 30 per cent at 20–30 cm depth, declining to *c.* 15 per cent at the top and bottom of the upper section. Within the lower section low-Mg calcite averages 13 ± 3.7 per cent, with a possible trend to lower values with depth.

Considering core A, the highest percentage low-Mg calcite occurs near the surface, with values declining from 14 per cent near the surface to as little as 6 per cent near the base of the upper section. However, in the lower section this trend reverses and low-Mg calcite content increases again to 13 per cent at the base of the core. In core B, low-Mg calcite appears to be a product of stabilization of both high-Mg calcite and aragonite in broadly equal proportions. However, in the less diagenetically mature core A, low-Mg calcite derives largely from high-Mg calcite in the upper section of the core, and from aragonite in the lower section.

Porosity data for each of the cores are presented in Figure 2D. Overall, core B has a significantly higher porosity than core A, with average values of 58 ± 7 per cent and 50 ± 5 per cent respectively, and this difference is particularly marked in the upper part of the profile. Mineral stabilization thus appears to be a non-conservative process, with net loss of calcium carbonate from the system. From the ground surface to a depth of about 60 cm there is a decrease in porosity with depth at a rate of *c.* 5 per cent/10 cm in both cores. Below a depth of 65 cm the two cores exhibit a similar rate of change of *c.* 5 per cent/10 cm, but markedly different trends in the vertical distribution of porosity. In core B porosity decreases with depth, while in core A the trend in the upper part is reversed and porosity increases to the base of the core. Overall there is a clear positive relationship between low-Mg calcite and porosity, even to the extent that the reversal of the depth dependence in the lower part of core A is apparent in both diagenetic products. The predominant control on total porosity thus appears to be diagenetic rather than depositional, with stabilization generating significant additional porosity. Given that changes in pore-size distribution are likely to be associated with changing total porosity, these trends are likely to promote significant differences in hydrological response between the cores.

It is possible that the dune has built seaward with a number of episodes of deposition, and more diagenetically mature sands (including site B) at the back of the dune complex may have been exposed to the meteoric environment for a longer period of time (studies are in progress). Furthermore, there are a number of environmental differences between the two sites which will promote more extensive diagenesis at site B. Within the vadose zone mineralogical stabilization will be enhanced where high moisture contents are maintained. Given the shallow depth of the water table at site B, this factor alone might explain the variation between the two cores and within core B. While mineral-controlled reactions are driven simply by the differences in thermodynamic stability, a number of additional drives for dissolution may be important. Rates of diagenetic processes will be enhanced and stabilization efficiencies reduced by carbonic and organic acids generated by biological activity within the sediment, the former controlling the partial pressure of carbon dioxide ($p\text{CO}_2$) with which the ground air and percolating waters equilibrate. Thus colonization of newly exposed or deposited sediments by a vegetation succession will result in progressive build-up of organic matter,

elevated $p\text{CO}_2$ and greater potential for stabilization.

As indicated by field inspection, at all depths core A has a much lower percentage of organic matter than core B, averaging 4.5 ± 2.0 per cent and 1.6 ± 1.0 per cent respectively (Figure 2E). Both cores show a significant increase in organic matter towards the surface, this being more marked in core B, where in the upper 10 cm the organic matter content increases to more than five times that of core A at comparable depths. This can be attributed both to a higher input of vegetative matter from the surface at site B, and also to the greater mixing and incorporation of litter observed in the field. In both cores there are abrupt vertical discontinuities in organic matter distribution. In core A, for example, the percentage of organic matter is 2.8 ± 0.3 per cent at depths less than 33 cm, but below this declines abruptly to 0.8 ± 0.3 per cent. Similarly, in core B the profile is complex, with abrupt boundaries at 10, 30 and 50 cm depth. The greater abundance of organic matter and presence of large roots at site B indicates higher levels of CO_2 and organic acids, both well known agents of carbonate dissolution. While organic matter concentrations and biogenic production of CO_2 are greatest at the surface, diffusive loss of CO_2 means that $p\text{CO}_2$ are low at shallow depths. Measured soil-air $p\text{CO}_2$ increases with depth below the surface at a rate of $c. 0.3$ per cent/10 cm at site B, reaching a maximum of 0.65 per cent at 20 cm, below which conditions are too moist for the probe to operate. In core A the rate of increase of CO_2 with depth is a maximum 2.2 per cent/10 cm in the upper 10 cm, and declines with depth approaching a constant 0.6 per cent CO_2 below $c. 60$ cm. Thus higher soil-air $p\text{CO}_2$ extending to shallower depths in core B provides an important additional drive for dissolution.

Finally, mixing of waters of differing $p\text{CO}_2$ or salinity will enhance dissolution due to the non-linearity in equilibrium calcium concentration (Plummer, 1975). Within Pleistocene limestones of the Bahamas this process is important in driving calcite dissolution in fresh-salt water mixing zone (Smart and Whitaker, 1988), although aqueous geochemical modelling suggests the role of mixing in the vadose zone is insignificant due to short residence times (Whitaker, 1992). However, the much higher fraction of unstable minerals in the Holocene sands, together with longer residence times, means that mixing may be important. Rainfall, equilibrated with atmospheric $p\text{CO}_2$, will mix with high $p\text{CO}_2$ pore waters as it percolates through the sands. In addition, inputs of dissolved salts may occur either by capillary rise from the water table, which is known to be brackish at site B, or by sea spray. While the latter has been suggested by Gardner and McLaren (1993) to be important in cementation of Malorcan aeolianites, the enhanced diagenesis above the water table in core B supports the case for the former.

DIAGENETIC CONTROLS ON HYDROLOGICAL BEHAVIOUR

Given the redistribution of calcium carbonate and changes in the nature and extent of porosity which occur as a result of diagenetic stabilization, it is improbable that the hydrological behaviour of the sands will remain unaffected. We have investigated two fundamental properties of the vadose zone hydrology of the sands: their moisture retention characteristics and hydraulic conductivity.

Moisture retention characteristics

Moisture retention curves derived from the pressure plate extraction tests reveal two statistically distinct groups (Figure 3A). All samples from core A have lower volumetric moisture contents at any given suction compared with those from core B, equivalent to $0.2 \text{ cm}^3 \text{ cm}^{-3}$ at 10 cm suction and increasing to $0.3 \text{ cm}^3 \text{ cm}^{-3}$ at 900 cm suction. Generally, core B sediments are composed of a greater proportion of larger pores which empty at low suctions, while core A has more relatively fine pores. This contrast exists at all depths within the cores, as seen from the vertical profiles of the moisture retained at suctions of 10 cm and 900 cm (Figure 3B). The role of diagenesis in controlling soil moisture tension is apparent in both cores. In core A there is a trend towards lower values in the upper 65 cm as porosity decreases and low-Mg calcite increases, and the trend reverses below this to the base of the core. Similarly, in core B there is a clear shift towards lower moisture content with depth, which occurs at an increased rate below 65 cm where porosity also decreases and low-Mg calcite increases more rapidly.

In both cores, at those depths where the extent of diagenesis is less, the moisture difference between the two suctions is also decreased. This is to be expected since samples of lower porosity have steeper curves as the

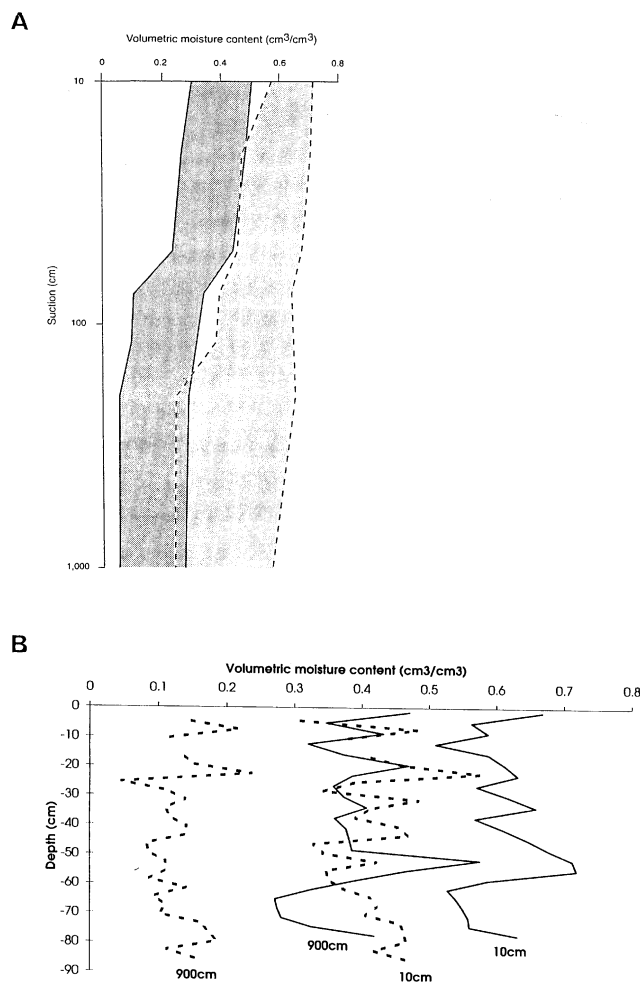


Figure 3. (A) Range of soil moisture characteristic curves. Dark stipple is core A, light stipple is core B. (B) Vertical variation in moisture retained at 10 cm and 900 cm suction. Broken lines are core A, solid lines are core B

proportion of large relative to small pores declines. Plotting the moisture retained at a given suction against percentage low-Mg calcite and porosity, for example at 900 cm suction, clearly shows the differences between the two cores (Figure 4). The low-Mg calcite content is a general indicator of diagenetic maturity, with higher values for core B associated with higher, if more variable, volumetric moisture content. However, the significant positive relationships between porosity and volumetric moisture content for both cores indicates that it is the change in porosity rather than the volume of stabilized material that is the critical control, supporting the findings of other work in different sediment types (Hall *et al.*, 1975; Arya and Paris, 1981; Rawls *et al.*, 1982). At a suction of 900 cm there is an increase in volumetric moisture content of 0.1–1.2 cm³ cm⁻³ with an increase in porosity from 40 to 70 per cent. The scatter in the plot reflects the influence of additional factors which affect the soil moisture retention curve, such as the grain-size distribution. However, the moisture retention at a given porosity is significantly greater in core B as compared with core A, possibly reflecting differences in the pore-size distribution and/or the influence of soil organic matter.

Whilst in most soil systems porosity is generated predominantly by the physical translocation of fine grains deeper into the soil profile, in the majority of carbonate materials dissolution is likely to be far more significant. The enhanced porosity apparent in the upper section of core B should therefore be viewed as a product of diagenetic alteration since the time of deposition. Where dissolutional porosity generation is localized within individual allochems there will be little effect on effective porosity, as the intra-granular voids frequently

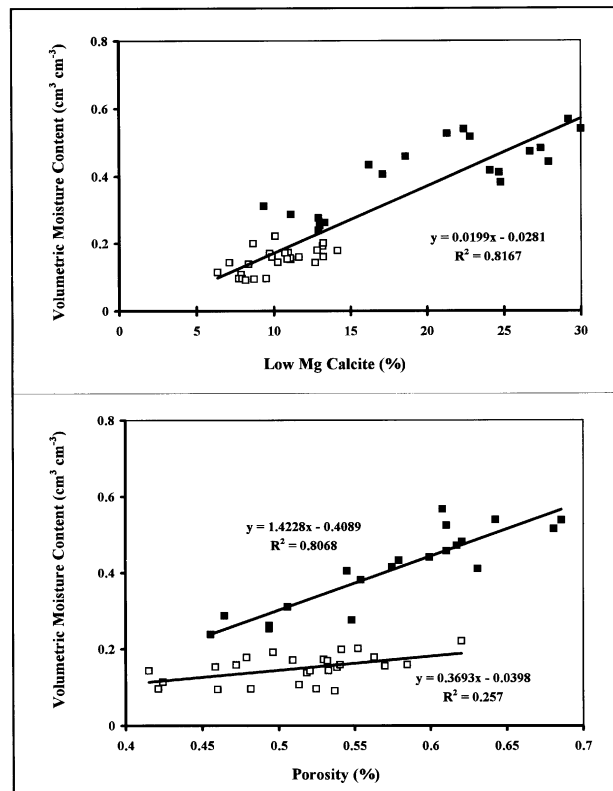


Figure 4. (A) Relationship between moisture retained at 900cm and percentage low-Mg calcite. (B) Relationship between moisture retained at 900cm suction and porosity. Open symbols are core A, solid symbols are core B

remain hydrologically isolated. However, dissolution of the outer surfaces of allochems will cause porosity to increase. This will occur more readily for fine grains that have a large surface area:mass ratio, those of bladed rather than spherical shape, and those with high surface roughness (Walter, 1986).

Both cores are composed of freely draining sand throughout their depth, but there are minor differences in particle-size distribution between the cores which may also be linked to their differing diagenetic maturity. Vertical profiles of the median grain diameter (D_{50}) show that core B is considerably more coarse-grained than core A (Figure 5). Once more, a contrast between the upper and lower section of core B is clear, and a lower D_{50} below a depth of 50 cm. The steady decrease in median grain size from the top of the core within the upper unit suggests that this cannot simply be explained by differing depositional sediment texture. These data support the suggestion that the extent of diagenetic stabilization declines with depth. Preferential dissolution of fine grains and/or aggregation of individual allochems bound by cements during mineral stabilization would result in a shift toward larger median grain size.

Core A, which has been subject to less extensive stabilization than core B, does not show the same trends or contrasts. There is an abrupt shift in grain size towards lower values at 50–60 cm depth, which is probably depositional in origin. The similarity between the upper part of core A and that of beach sands from the back-beach (eroding coastal margin of the dune) and foreshore suggests that site A may receive input of mineralogically unevolved sediments during periodic washover events which do not appear to have affected site B. Interactions between depositional processes, diagenesis and vadose zone hydrology are the subject of ongoing field and laboratory studies.

Hydraulic conductivity

Direct measurement of the saturated hydraulic conductivity of all sub-samples revealed considerable

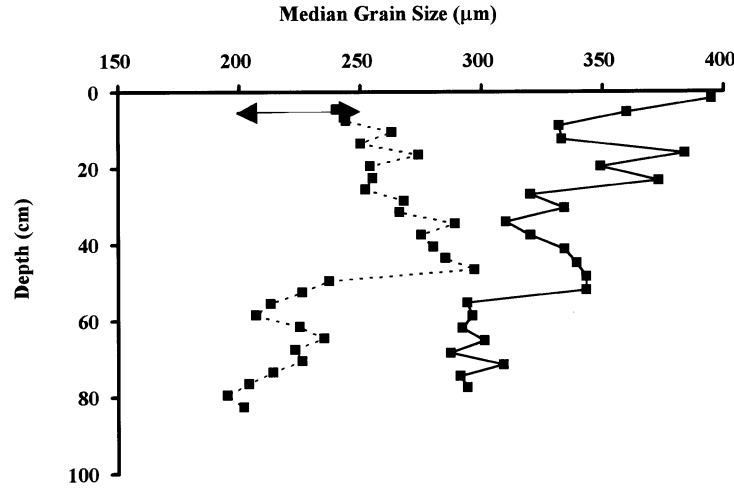


Figure 5. Vertical variation in median grain size (D_{50}). Broken line is core A, solid line is core B; arrow shows range of modern beach sands sampled

variability, values ranging from 3×10^{-5} to $9 \times 10^{-4} \text{ ms}^{-1}$, with a median of $1 \times 10^{-4} \text{ ms}^{-1}$. These relatively high values are consistent with the sandy nature of the sediments, and agree well with other published data for Bahamian Holocene sands (Budd, 1984; McClain *et al.*, 1992). It might be expected that core B, with its higher porosity and coarser grain size, would be more permeable (Masch and Denny, 1967; Uma *et al.*, 1991), but intra-profile variability masks this. The small number of anomalously high permeabilities may be due to the presence of root channels within the individual sub-samples, and there appears to be a general increase in permeability towards the top of both cores, this effect extending to greater depth in core B where the extent of diagenesis is greater.

However, unsaturated hydraulic conductivity, and its response to varying suction, is difficult to measure, especially for small samples. There are many models available which derive this relationship for materials of differing porosity and grain size (e.g. Millington and Quirk, 1959; Van Genuchten, 1980). Here we use the method of Campbell (1974) as the required parameters have been directly measured for the samples. Essentially, the soil moisture characteristic curve above the air entry suction, or bubbling pressure, is described by a simple relationship given by the following equation:

$$\psi = a \left(\frac{\theta_{sat}}{\theta} \right)^{-b} \quad (1)$$

where ψ = suction (m), θ = volumetric moisture content ($\text{cm}^3 \text{cm}^{-3}$), θ_{sat} = saturated moisture content ($\text{cm}^3 \text{cm}^{-3}$), and a and b are empirical parameters. For each of the retention curves described above, values for the a and b parameters were found. Figure 6A plots the a parameter against the b parameter for all samples. Samples from the two cores fall into distinctive groups, with core B having generally lower values for both parameters. These groupings reflect the changes in shape and position of the moisture retention curves. The a parameter is the logarithm of the lowest suction reached before volumetric moisture content effectively becomes equal to saturated soil moisture content, and represents the probable air entry suction. Values for air entry suction found from the logarithm of a range from 0.32 to 12 cm for core A and 1 to 100 cm for core B. While these are low suctions for air entry compared with other types of material, the range of values is consistent with those frequently reported for sandy sediment (Campbell, 1974; Saxton *et al.*, 1986; Hendricx, 1991). The b parameter gives the rate of increase in suction with decrease in moisture content for the suction range above the air entry

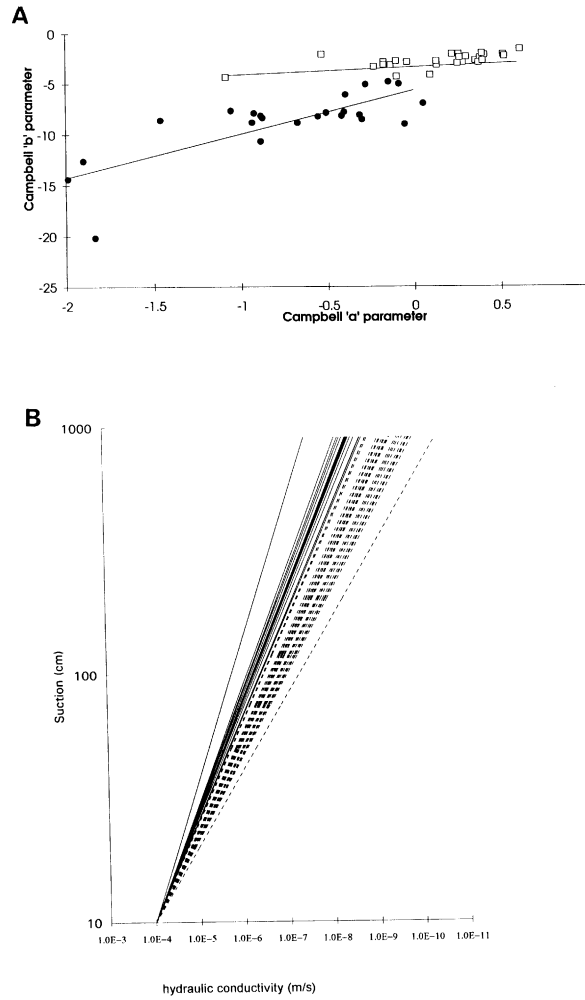


Figure 6. (A) Relationship between Campbell parameters a and b . Open symbols are core A, solid symbols are core B. (B) Relationship between modelled soil suction and unsaturated hydraulic conductivity. Solid lines are core A, broken lines are core B

value. Given that the value of b is negative in Equation 1, all samples from core B have larger exponents than those from core A, so larger suctions will develop for a given moisture content.

Using this model it is possible to establish the changes in unsaturated hydraulic conductivity at a range of suctions resulting from diagenesis. The relationship between suction and hydraulic conductivity can be described by the following equation:

$$k_{unsat} = k_{sat} \left(\frac{\psi_e}{\psi} \right)^{2 + \frac{2}{b}} \quad (2)$$

where k_{unsat} = unsaturated hydraulic conductivity (m s^{-1}), k_{sat} = saturated hydraulic conductivity (m s^{-1}), ψ_e = air entry suction (m), ψ = suction (m) and b is the same as in Equation 1. The median value of measured saturated hydraulic conductivity was employed here, together with the b parameter calculated as described above for each sample. ψ_e is the air entry suction, which can be taken to be about 10 cm in these sandy materials. The relationship between unsaturated hydraulic conductivity and suction for each of the samples was derived and the results are presented in Figure 6B. Again, samples from the two cores form two distinct groupings. Starting

from the same hydraulic conductivity at saturation, core A has a more pronounced rate of decline in hydraulic conductivity with increased suction than core B. At a suction of 900 cm there is an average difference in hydraulic conductivity of about two orders of magnitude between the two cores, reflecting variations in pore-size distributions. Within this suction range (10–1000 cm) it is the larger pores which are water-filled. The lower porosity and finer grain-size distribution of core A results in fewer large pores and lower hydraulic conductivity. This gives a smaller cross-sectional area of conducting voids and lower flux of water through the sediment for a given hydraulic gradient. In comparison, core B has more large pores which conduct moisture faster at these low suctions. As suctions increase, the differences between hydraulic conductivity in core A and core B become more pronounced.

The implication of this calculation is that residence times for water in the vadose zone at site A may be longer than for site B, which has higher permeability in an unsaturated state. This is particularly significant given the seasonality of the Bahamian climate, together with the episodic and intense nature of the majority of storm events. Thus sediments with a larger proportion of smaller pores, whether due to differences in depositional texture or to diagenetic modification, will retain moisture for longer and be subject to enhanced rates, and possibly also higher efficiency, of mineral stabilization.

CONCLUSIONS: THE CO-EVOLUTION OF HYDROLOGICAL BEHAVIOUR AND DIAGENESIS

This study focused on a beach ridge of late Holocene age, consisting of a high proportion of metastable high-Mg calcite and aragonite with rapid reaction rates and situated in the relatively wet northern Bahamas. We have presented new data which demonstrate the role of diagenesis in controlling moisture retention characteristics in mixed mineralogy carbonate sands. Although these sediments are still mineralogically relatively immature, significant alteration has occurred, with sands at site B more diagenetically evolved, especially at shallow depth, than those at site A. This maturity is expressed by the increase in low-Mg calcite fraction, and an increase in porosity due to dissolution of allochems. There are two possible reasons for the strong contrasts observed in the extent of diagenesis between the two cores. Firstly, diagenetic rates operating at the two sites may differ, with stabilization being more rapid in the moister conditions of site B, where organic content and $p\text{CO}_2$ are higher and mixing is also likely to be of significance. This would also account for vertical variations at site B. Alternatively, if the dune has accreted seaward, sands at site A may be younger, and thus have been exposed to the meteoric realm for less time. This question may be resolved by ongoing investigation of rates of diagenesis and radiocarbon dating of the unaltered mineral fraction.

Mineral stabilization results in changes in total porosity and pore-size distribution which have important implications for hydrological behaviour. In the suction range considered, diagenesis has resulted in more moisture being retained at a given suction. However, the influence of changing vadose zone hydrology is also exerted through changes in the unsaturated hydraulic conductivity–suction relationship. In a stabilized carbonate continued diagenesis requires a large flux of water to provide reactants and remove products. Where there are inherent thermodynamic drives, as in the case of mineral-controlled reactions, the rate of reaction is dependent upon the presence of a fluid medium. Thus, residence times affect the transformation of aragonite and high-Mg calcite to low-Mg calcite and, over time, changes in vadose zone hydraulic conductivity will lead to changes in residence times. It is important to establish whether stabilization leads to longer or shorter residence times, as the former will enhance porosity generation in a positive feedback process, whereas the latter will result in a slowing of stabilization with increasing geochemical evolution of the system.

The study has demonstrated that although diagenetic modifications to the pore network result in an increase in hydraulic conductivity, especially at high suction, moisture retention will also be increased. We suggest that this may significantly enhance mineral-controlled reactions, giving rise to positive feedbacks. However, the effect of evolving hydrological behaviour on water-controlled reactions is less clear. Water retained in the pores will have time to better equilibrate with soil-air CO_2 , increasing net dissolution, but the majority of recharge waters will pass through the vadose zone more rapidly without interacting with the mineral phases. This water will thus reach the water table relatively unaltered, where it will mix with phreatic waters and equilibrate with soil air CO_2 , localizing diagenesis at the top of the fresh-water lens.

We can thus envisage important process–response feedback mechanisms, whereby stabilization reactions

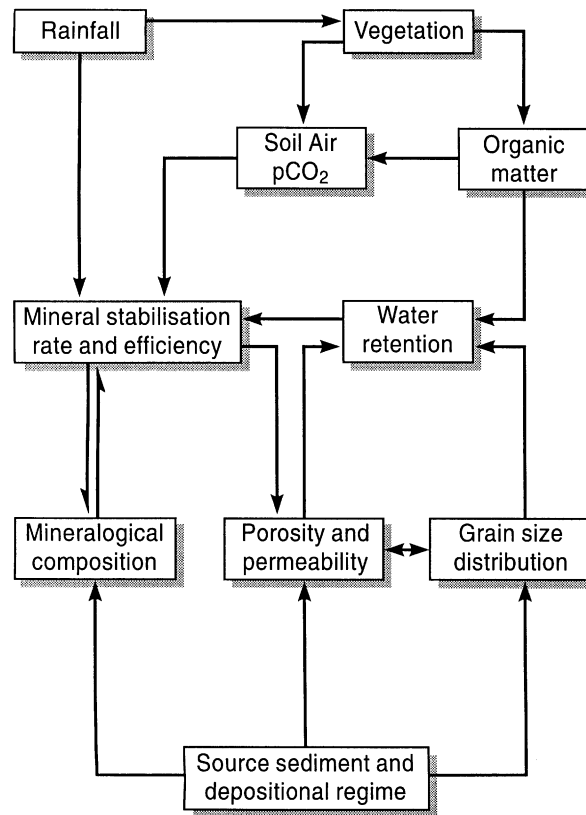


Figure 7. Process–response diagram illustrating positive feedback mechanisms in the co-evolution of vadose zone hydrology, poro-perm characteristics and mineralogy in carbonate sediment

modify the pore network, affecting moisture retention and subsequent diagenesis (Figure 7). The mineralogical composition of sediment and its pore-size distribution and connectivity are a function of the efficiency and rate of mineral stabilization, as well as the total time spent in the vadose zone. Stabilization efficiency and rate are generally recognized to be controlled by total recharge and geochemical potential for water-controlled reactions which is enhanced by high soil-air $p\text{CO}_2$. However, both water- and to a greater extent mineral-controlled reactions also depend on the residence time of water within the pores. Moisture is retained preferentially within smaller voids at high suctions, and at low suctions closer to the water table. Each exerts a control on subsequent diagenesis. The pore characteristics (total porosity, pore-size distribution and connectivity) are thus critical and are dependent upon the primary depositional grain-size distribution and on diagenetic modifications by dissolution and cementation. In addition, pedological development will affect not only geochemical diagenetic drive but may also significantly affect water retention characteristics. Clearly there is a need for further research to test this process–response model. It is important to establish how such interactions operate in different environments and over different time scales if we are to understand more fully the evolution of poro-perm characteristics in young carbonates.

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